03-67-101

PERIODIC PROGRESS REPORT NO. 2

for

SOLAR-CELL INTEGRAL COVER-GLASS DEVELOPMENT

for the period

June 1, 1967 to August 31, 1967

Contract No. NAS5-10319

Prepared by

TEXAS INSTRUMENTS INCORPORATED
COMPONENTS GROUP
P. O. Box 5012
Dallas, Texas 75222

for

NASA-GODDARD SPACE FLIGHT CENTER
Glenn Dale Road
Greenbelt, Maryland

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SUMMARY

This report presents second-quarter progress on a 12-month research and development program for applying integral cover-glass coatings to silicon solar cells by radio-frequency sputtering, performed under contract NAS5-10319 for the NASA-Goddard Space Flight Center.

Integral coatings of 7940 fused silica up to 4.2 mils have been deposited during this period. Sputtering equipment modifications have increased the deposition rate and uniformity. Deposition rates as high as 2400 Å/min (0.57 mil/hr) have been observed on this equipment.

The majority of the work in this reporting period was directed toward developing the anti-reflective coating between the silicon solar cell and the integral 7940 fused-silica coverslide. Solar cells coated with nominal 575 Å of CeO_2 consistently have shown an increase in conversion efficiency after integral coating. Sunlight data should show the CeO_2 integrally-coated cell to be more efficient than the standard, silicon-monoxide-coated cells without protective covers.

Two-mil thick, integral-coated cells showed no significant changes in electrical parameters or physical characteristics after being subjected to a thermal-cycling test from +100°C to -100°C. Ultraviolet exposure tests on cells with integral coatings up to 2-mil thickness indicate that the RF-sputtered quartz films are effectively impervious to this short wavelength radiation. The short-circuit current of these test cells decreased less than an average 0.2 percent; which is within the reproducibility limits of the tungsten light source.

Stress measurements on RF-sputtered SiO_2 films on silicon cells have been extended up to 4.16-mil film thickness. The observed stresses are compressive and range from 2000 to 6000 lbf/in^2.

Radio-frequency sputtering has proven to be the best reported technique for applying integral covers on silicon solar cells. Low-stress quartz films of high-optical quality can be applied to solar cells at high deposition rates with no significant degradation to the cell characteristics. Production-size runs can be coated with 1-mil-thick covers in less than two hours operating time.

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SECTION I
INTRODUCTION

A. OBJECTIVE

The objective of this contract is to conduct a 1-year research-and-development program for applying integral cover-glass coatings to silicon solar cells by radio-frequency sputtering. The primary objectives for applying integral coatings to solar cells are: 1) to eliminate adhesive between cell and cover-glass which 2) removes the requirement for ultraviolet rejection filters on underside of cover-glass; 3) to increase power-to-weight ratio of cell/cover-glass assembly on missions which require less than 6-mil filters; 4) to reduce cost of present solar-cell/cover-glass combination. It is advantageous to eliminate the adhesive, since most adhesives darken under ultraviolet (u-v) radiation and are limited to a maximum temperature range of approximately 200°C. It has been demonstrated that radiation damage in silicon solar cells can be annealed-out by subjecting the cell to approximately 400°C for brief periods.[1/]

B. SCOPE OF WORK

This development program involves deposition of integral quartz coatings directly on silicon solar cells by radio-frequency sputtering. Coatings, to be applied directly to the cell without subjecting it to temperatures in excess of 500°C, are to be in the thickness range of <1-to-20 mils. Integral-coated cells will be tested, both optically and environmentally, with conventional 6-mil 7940 quartz coverslide cells as a control group. The program should yield an integral cover-glassed solar cell which, pricewise, is competitive under present-day production methods. Integrally cover-glassed sample cells will be supplied to NASA on scheduled dates during the contract.

[1/] Fang, P. F., Proceedings of the Fifth Photovoltaic Specialists Conference (October 1965).

SECTION II
TECHNICAL DISCUSSION

A. R-F SPUTTERING APPARATUS

A review of the techniques used for the deposition of insulator films on silicon and a theoretical discussion of radio-frequency sputtering was presented in Periodic Progress Report No. 1 for the subject contract. A detailed description of the critical process variables was also presented. During this reporting period, several important changes were made in the equipment which resulted in a higher deposition rate.

The equipment used during the first four months of the contract is shown in Figure 1. Note the large, electromagnet concentric with the bell jar. However, the magnet was not concentric with cathode assembly, which was offset on the base plate due to the vacuum port as is illustrated in Figure 2. The normalized flux density as a function of the radius of the electromagnet coil is illustrated in Figure 3. The non-concentric cathode/magnet arrangement resulted in a non-uniform magnetic-flux density across the cathode assembly, which contributed to the non-uniform deposition rate.

The highest deposition rate obtained on this contract with this "first generation" equipment was 2100 Å/min, with approximately 75-percent uniformity over the working area of the substrate holder. The majority of the runs on this equipment averaged between 1200 and 1600 Å/min with the 7940 fused-silica target as the source.

The temporary set up for the "second generation" sputtering system is illustrated in Figure 4. The major change in the system is the concentricity of the cathode assembly with the bell jar, and

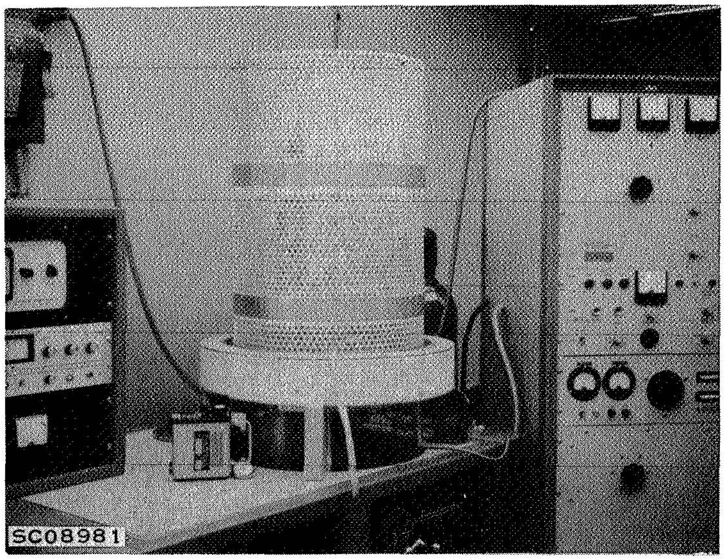

Figure 1. RF Sputtering System (First Generation)

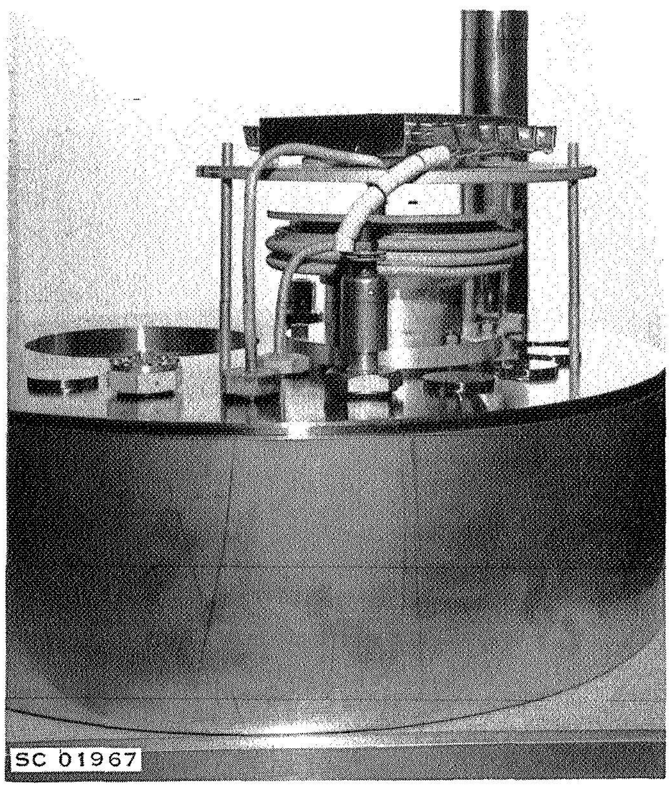

Figure 2. Electrode Assembly for RF Sputtering System (First Generation)

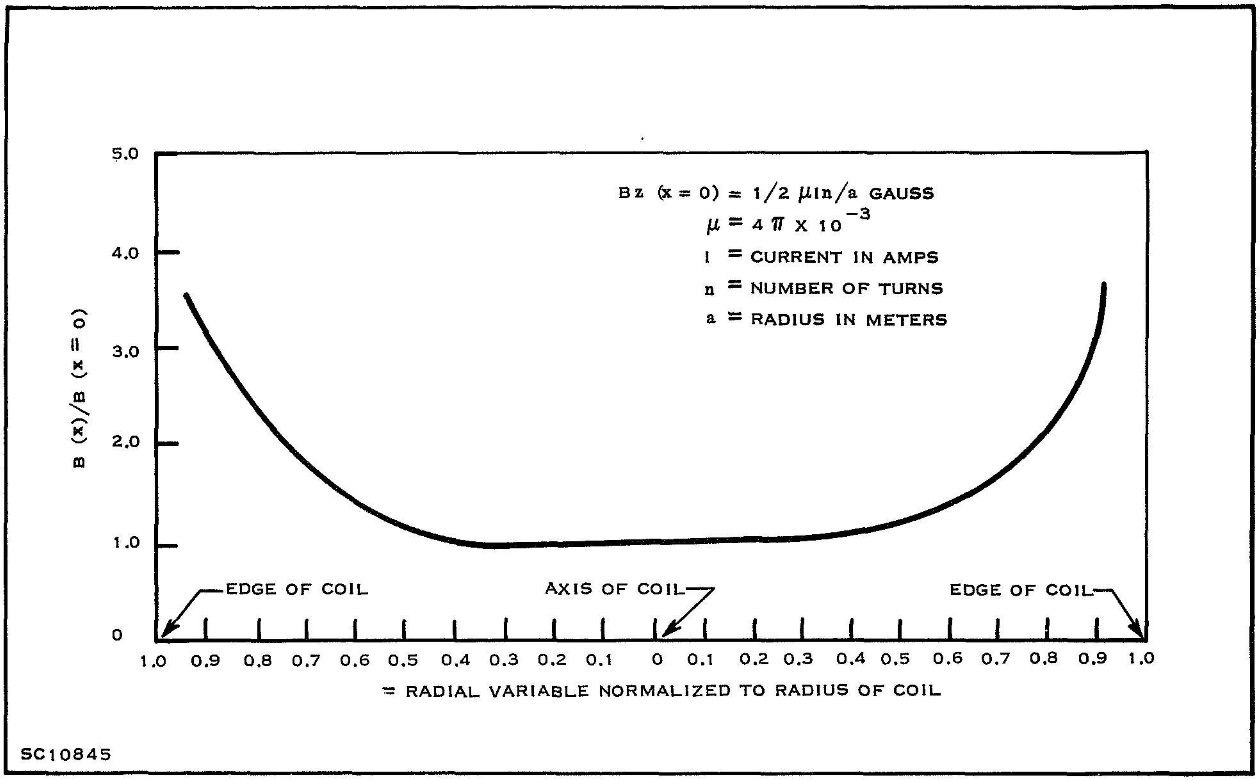

Figure 3. Normalized Magnetic Flux Density versus Normalized Radius of Electromagnet Coil

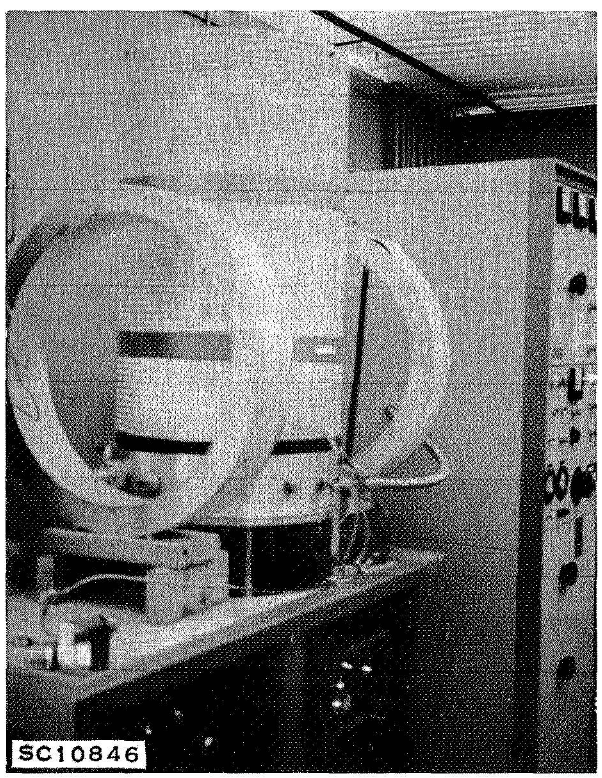

Figure 4. RF Sputtering System (Second Generation)

the utilization of the Helmholtz configuration of the electromagnets. The details of the cathode assembly with the associated cooling coils and substrate assembly are illustrated in Figure 5. The 7940 fused-silica target is shown directly on the cathode with the substrate holder approximately 1-inch above. Deposition rates as high as 2400 Å/min have been achieved with this arrangement while the majority of the runs averaged from 1400-to-1800 Å/min. With this arrangement, the uniformity was improved to approximately 80-percent across the working area of the substrate holder. For example, on a typical 2-1/2-hour run, the integral thickness would range from 0.8-to-1 mil.

B. ANTI-REFLECTIVE COATINGS

The majority of the work in this reporting period was directed toward optimizing the optical coating between the silicon and the sputtered-quartz layer. An evaporator was modified to deposit films by evaporation from a hot-filament arrangement. Since cerium dioxide exhibits the desired refractive index of approximately 2.3 when properly deposited, it was selected for the initial evaluations. Although the first coatings were fairly soft, additional experimentation yielded CeO_2 coatings of hardness equal to standard production SiO coatings. The reflectance of a CeO_2-coated cell as compared with a SiO-coated cell is illustrated in Figure 6. The SiO-coated cell was visibly selected with a coating of virtually the same optical thickness for comparison. As expected, the reflection from air to the CeO_2-coated cell is higher than the SiO-coated cell.

Si_3N_4 was also investigated as an intermediate, anti-reflective coating. The films were deposited by RF sputtering from a Si_3N_4 target in argon, oxygen, and nitrogen ambients. The refractive indices of the films varied from 1.9 to 3.2 depending on the deposition techniques. Integral coatings were not deposited over these films since the desired refractive index and film thickness was not achieved, and the process for the CeO_2 coatings was acceptably reproducible.

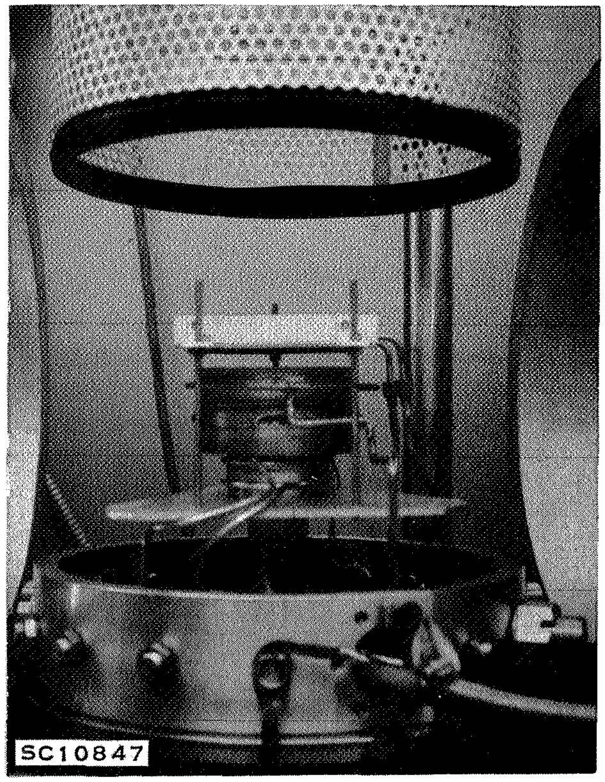

Figure 5. Electrode Assembly for RF Sputtering System (Second Generation)

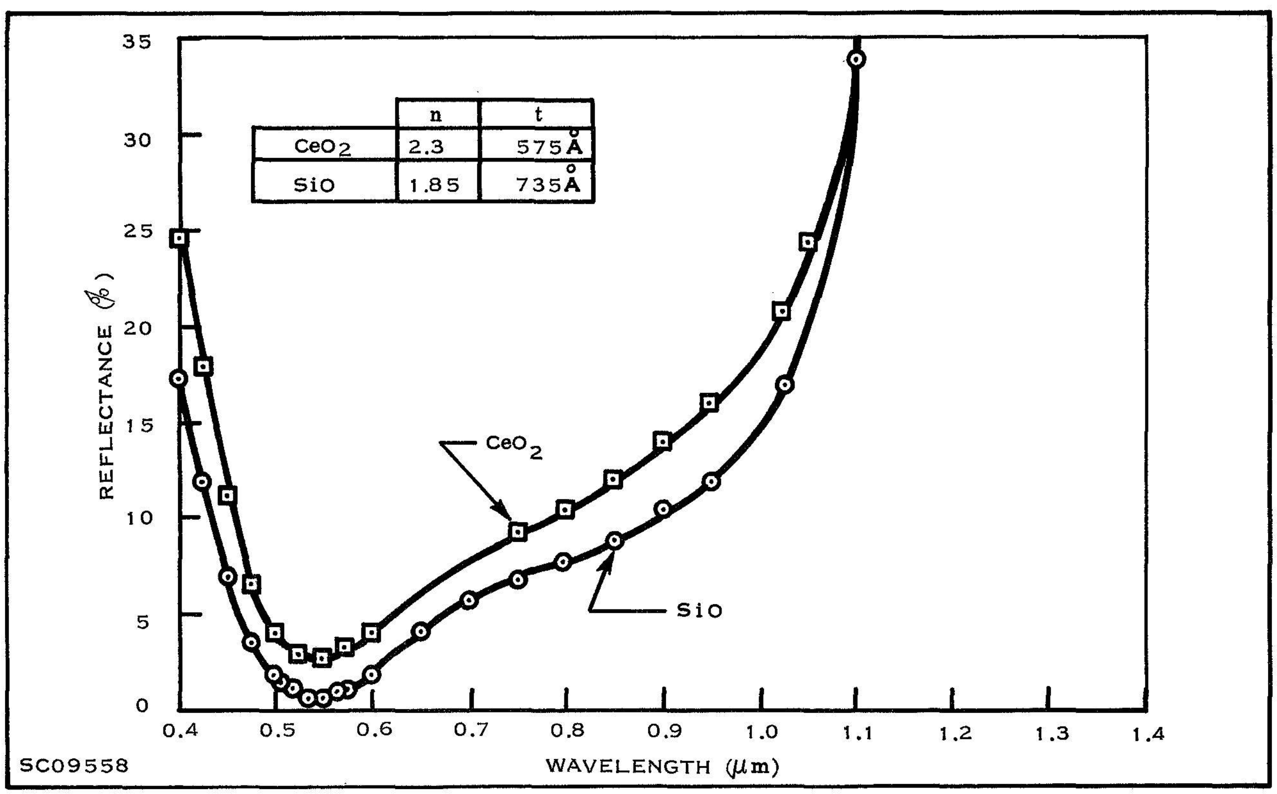

Figure 6. Reflectance of CeO_2 and SiO-Coated Silicon Solar Cells

Reactive RF sputtering of Si_3N_4 was not attempted as planned since the only silicon target available was 4 inches in diameter, which was not compatable with the current 6-inch diameter cathode assembly.

C. INTEGRAL COATINGS

Integral coatings of 7940 fused silica up to 4-mil thickness were deposited on both SiO- and CeO_2-coated cells by RF sputtering. The optical characteristics of the cells were evaluated before and after integral coating. The reflectance of a CeO_2-coated cell before and after integral coating of 1-mil thickness is illustrated in Figure 7. The integral coating was deposited at a rate of 1600 Å/min. The reflectance of the cell was reduced by the application of the integral coating as predicted by theory. A comparison of the reflectance of a CeO_2 and a SiO anti-reflective-coated cell after 1-mil integral coatings is illustrated in Figure 8. The increased reflectance of the CeO_2-coated cell in the region of 1.0-to-1.2 μm is caused by the chemically-polished P-contact surface of the cell, which effectively reflects the longer wavelength radiation. The SiO-coated cell had a sawed P-contact surface, which highly absorbs and disperses the 1.0-to-1.2 μm radiation. The significant part of the plot is the 0.4-to-1.0 μm region. It shows the reduced reflectance of the CeO_2-coated cell over the SiO-coated cell after the integral-coating operation.

The efficiency of the CeO_2-coated cell should improve after integral coating, if the integral film has "good" transmission characteristics and the cell is not damaged in the coating process. A set of I-E curves, which show the typical power increase realized after integral coating over a CeO_2-coated cell, are illustrated in Figure 9. The output characteristics under tungsten light of 20 CeO_2-coated cells before and after integral coating of nominal 1.4-mil thickness are listed in Table I. It should be noted that the data were taken under a tungsten light source which was calibrated

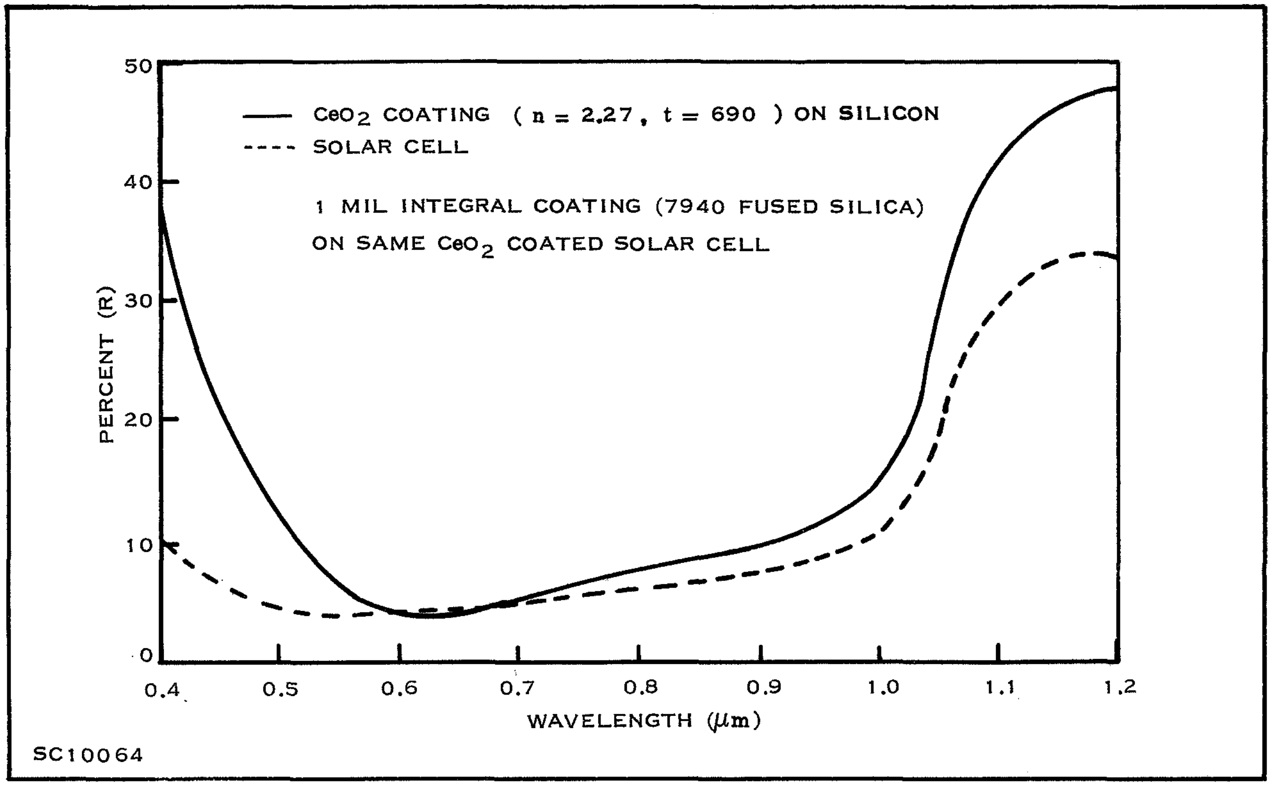

Figure 7. Reflectance of CeO_2-Coated Silicon Solar Cell Before and After Integral Coating

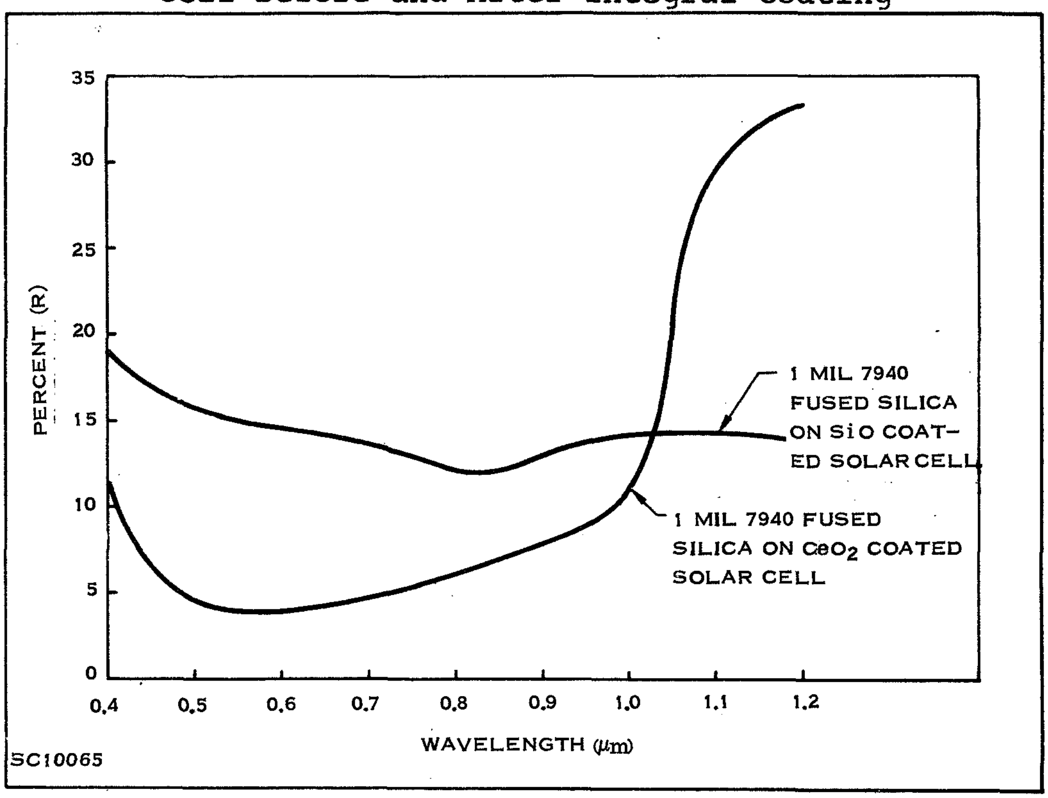

Figure 8. Reflectance of Integrally-Coated Solar Cell with SiO and CeO_2 Anti-Reflective Coatings

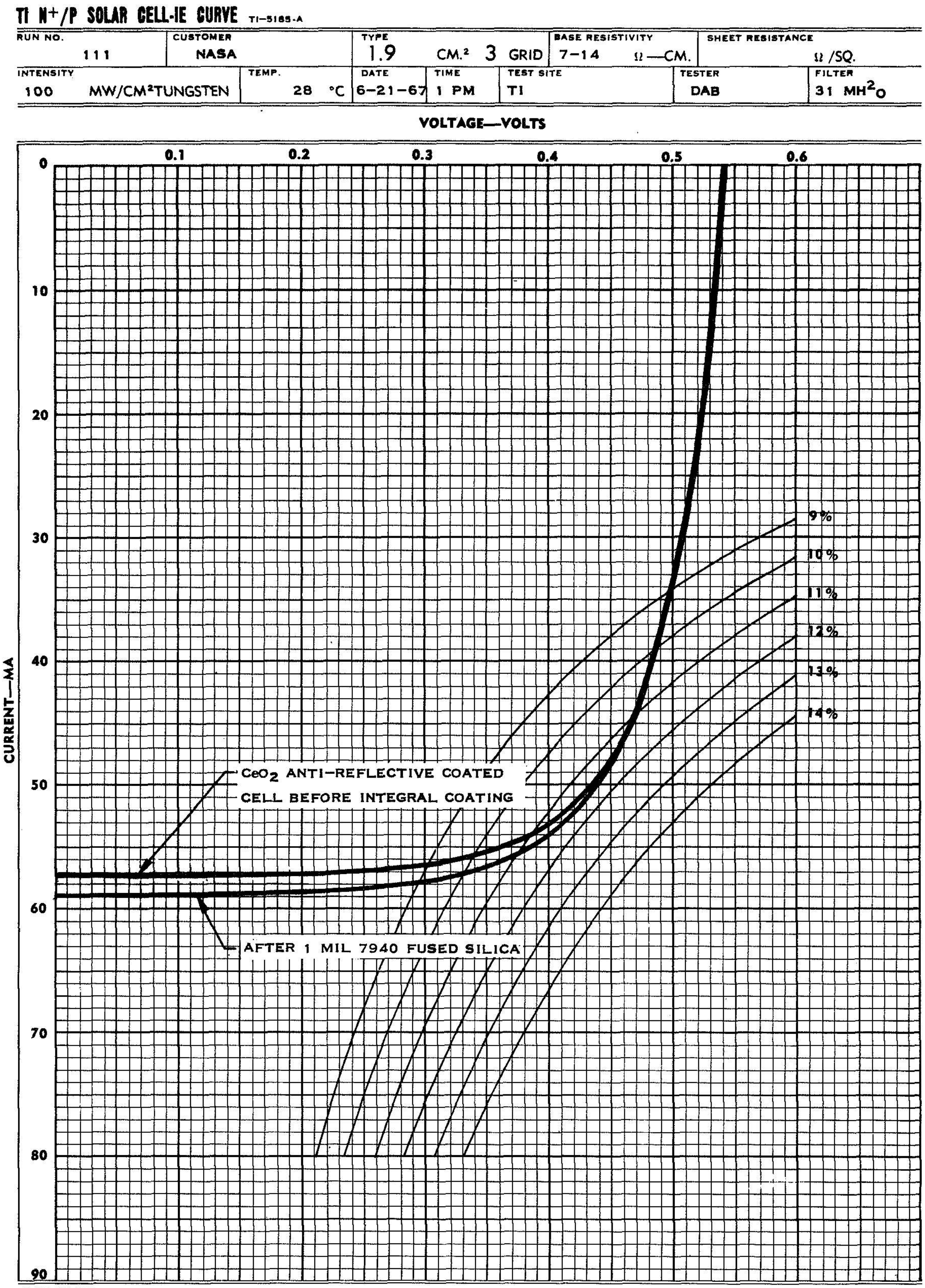

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Figure 9. I-E Curve of CeO_2 Anti-Reflective Coated Silicon Solar Cell Before and After Integral Coating

Table I. Electrical Characteristics of Solar Cells Before and After Integral Coating

Cell No.	ISC (mA)			I at 0.430 V (mA)			V_{oc} (mV)		
	After CeO_2	After Integral	Δ	After CeO_2	After Integral	Δ	After CeO_2	After Integral	Δ
62	59.8	60.8	+1.0	52.0	52.0	0	545	545	0
65	59.2	60.5	+1.3	51.5	51.5	0	542	542	0
67	57.0	57.8	+0.8	50.0	50.9	+0.9	545	545	0
68	58.0	59.0	+1.0	51.0	51.5	+0.5	542	542	0
71	58.0	60.5	+2.5	50.0	53.0	+3.0	542	542	0
72	58.5	59.0	+0.5	49.9	52.0	+2.1	542	545	+3
73	57.0	59.0	+2.0	50.3	52.0	+1.7	548	548	0
75	58.0	60.0	+2.0	51.0	52.5	+1.5	545	548	+3
79	57.5	59.8	+2.3	51.0	52.0	+1.0	547	547	0
82	57.8	60.8	+3.0	51.0	53.0	+2.0	542	542	0
83	58.5	61.0	+2.5	52.0	52.5	+0.5	548	540	-8
84	58.0	60.5	+2.5	51.0	52.0	+1.0	542	542	0
85	59.2	60.8	+1.6	51.5	52.5	+1.0	540	542	+2
86	58.5	60.5	+2.0	51.8	53.2	+1.4	542	542	0
87	57.8	60.2	+2.4	51.5	52.8	+1.3	548	548	0
89	58.0	60.5	+2.5	52.0	53.3	+1.3	549	549	0
90	57.2	60.2	+3.0	49.5	51.4	+1.9	540	540	0
91	60.0	61.3	+1.3	52.0	52.8	+0.8	542	542	0
92	59.2	61.0	+1.8	52.0	53.0	+1.0	548	548	0
93	58.0	60.2	+2.2	51.0	53.0	+2.0	542	548	+6
Average	58.3	60.2	+1.9	51.1	52.3	+1.2	544	544	--

with a SiO-coated, Table Mountain standard solar cell. The CeO_2-coated cells with integral coatings would exhibit higher conversion efficiency under a "blue" light source due to the low reflectance in the 0.4-to-1.0 μm region of the spectrum.

Integral-coated cells will be evaluated under sunlight and/or an AMO simulator data in the fourth quarter of the contract to determine the conversion efficiency of the cells accurately.

D. FILM STRESS MEASUREMENTS

Stress measurements on RF-sputtered SiO_2 films have been extended to thickness up to 4.16 mils, and previous results have been recalculated using Poisson's ratio to account for the stress involved in lateral deformation. The equation used was

$$\sigma = \frac{E_{si}\, t\, (t + Rd)}{6rd\, (1-\bar{v})}$$

where

σ = stress, lbf/in^2 (compressive film stress +)
E_{si} = elastic modulus of Si, $2.46 \times 10^7\ lbf/in^2$
t = substrate thickness, in.
d = film thickness, in.
$R = E_{SiO_2}/E_{Si} = 0.422$
r = radius of curvature, in.
$\bar{v}$ = Poisson's ratio, thickness-weighted mean.

The curvature of cells was measured optically, as described in the previous report. The data are summarized in Table II.

The variation of stress with film thickness is shown in Figure 10. The neat exponential decrease previously observed has been disrupted by an upturn at very large thicknesses. The shape of the curve fits no convenient simple function, so the data are presented in empirical form. Additional data must be obtained to verify this dependence and establish the approximate magnitude of random errors.

Table II. Summary of Cell Curvature

Cell No.	d, mils	t, mils	d/t	r, in.	σ, lbf/in^2
11	0.64	2.88	0.222	12.46	6024
9	0.25	3.18	0.236	13.80	5690
5	0.95	3.45	0.275	13.34	5698
2	1.15	3.10	0.321	12.46	4081
3	1.86	2.42	0.769	10.79	2052
4	1.03	2.80	0.368	13.21	3505
41	3.38	10.44	0.323	69.45	2845
64	4.16	12.36	0.337	67.77	3349

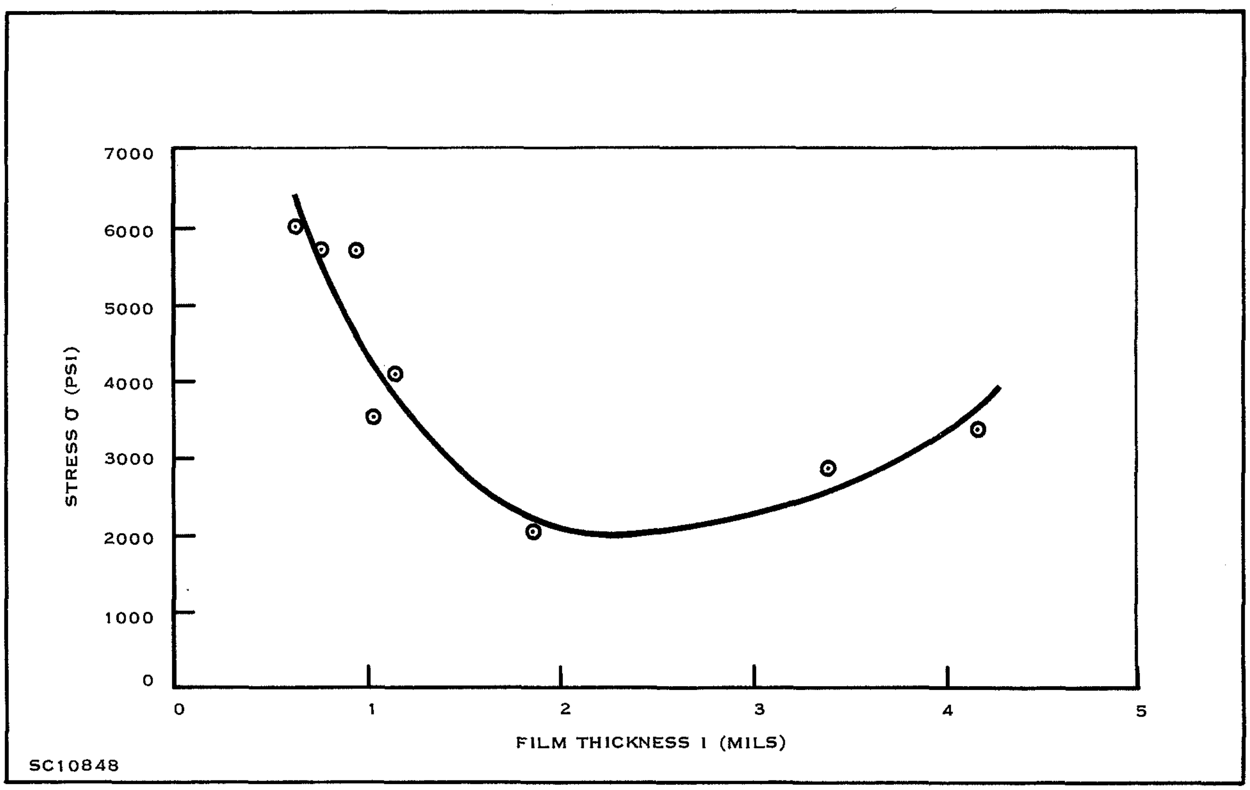

Figure 10. Stress versus Film Thickness

In any case, the observed stresses are all compressive and fairly small, ranging approximately from 2000-to-6000 lbf/in^2 (1.4-to-4.1 by 10^8 $dyne/cm^2$). These values are all far below the ultimate compressive strength of SiO_2, or the tensile strength of silicon, accounting for the observed absence of stress-induced mechanical failure.

Additional environmental testing on > 2-mil-thickness films will be required to determine if the film stress is a serious problem. The resultant curvature of the cells for integral films over 1- to 2-mil thickness may certainly cause problems in submodule fabrication.

E. ENVIRONMENTAL TESTING

1. Ultraviolet Exposure

An environmental test, which consisted of 500 hours of mercury vapor lamp exposure at 12.5 mW/cm^2 intensity, was performed on the following groups:

- Test Group: (Quantity - 4) CeO_2 anti-reflective coated cells with 7940 fused silica integral coatings of 0.8- to 2.0-mil thickness.
- Primary Control: (Quantity - 4) SiO-coated cells with 6-mil thickness, 7940 fused-silica coverslides (anti-reflective coated and 450-nm rejection filter), bonded with GE RTV 602 adhesive.
- Secondary Control: (Quantity - 5) SiO-coated cells with 6-mil thickness, 7940 fused-silica coverslides (uncoated), bonded with GE RTV 602 adhesive.

The results of this test are presented in Table III. The data were taken under a tungsten-light source and are presented not as absolute numbers, but to show the relative changes of the different cell groups under ultraviolet exposure. The largest change observed in the integral-coated cells was cell No. 99 (integral coating of 0.8-mil thickness), which lost 2.7 mA at 430 mV. It is interesting to note, that although the integrally coated cells dropped

Table III. Electrical Results of Ultra-Violet Exposure Test

Cell No.	Description	I_{SC} (mA)			I at 430 mV (mA)			V_{OC} (mV)		
		Initial	Post-Test	Δ	Initial	Post-Test	Δ	Initial	Post-Test	Δ
95	Integral 2.0 mils	59.5	59.5	0	51.2	50.8	-0.4	541	540	-1
98	Integral 1.3 mils	59.7	60.1	+0.4	52.0	51.1	-0.9	540	539	-1
99	Integral 0.8 mil	61.5	60.1	-1.4	52.8	50.1	-2.7	542	537	-5
100	Integral 1.1 mils	60.4	61.2	+0.8	52.1	52.1	0	545	541	-4
Avg.		60.3	60.2	-0.1	52.0	51.0	-1.0	542	539	-3
12	6-mil Uncoated Coverslide	57.0	55.2	-1.8	47.0	44.0	-3.0	539	535	-4
17	6-mil Uncoated Coverslide	57.0	54.9	-2.1	46.9	48.1	+1.2	532	530	-2
24	6-mil Uncoated Coverslide	57.6	55.1	-2.5	48.7	45.3	-3.4	528	521	-7
25	6-mil Uncoated Coverslide	57.9	55.6	-2.3	48.7	46.2	-2.5	531	529	-2
26	6-mil Uncoated Coverslide	58.2	57.5	-0.7	48.7	48.0	-0.7	532	529	-3
Avg.		57.5	55.6	-1.9	48.0	46.3	-1.7	532	528	-4
13	6-mil Coated Coverslide	57.8	58.0	+0.2	48.4	48.5	+0.1	535	534	-1
14	6-mil Coated Coverslide	57.9	57.7	-0.2	49.2	48.5	-0.7	535	530	-5
16	6-mil Coated Coverslide	57.2	56.8	-0.4	48.0	47.0	-1.0	535	529	-6
22	6-mil Coated Coverslide	58.1	57.4	-0.7	49.1	48.0	-1.1	535	532	-3
Average		57.8	57.3	-0.3	48.7	48.0	-0.7	535	531	-4

an average of 1.0 mA at 430 mV, the output of these cells was 3.0 mA higher than the primary control test cells, which lost 0.7 mA at 430 mV. The cells with the uncoated coverslides, which were included in the test to show the effect of ultraviolet radiation on the bonding adhesive, lost an average of 1.9 mA shortcircuit current; whereas, the integrally coated cells and the cells with coated coverslides lost 0.1- and 0.3-mA short-circuit current, respectively. Further ultraviolet tests will include uncoated coverslides with a minimum of 6 mils of RF sputtered, 7940 fused-silica coatings to determine the change in transmission of the coating from 0.4-to-1.1 μm.

2. Thermal Cycle

Thermal cycling was performed on both integrally-covered cells and standard production cells with 6-mil coverslides (coated). The temperature cycle was from room temperature to +100°C to -100°C to room temperature as shown in Table IV.

Table IV. Thermal Cycle Conditions

Phase	Transit Time-Min.	No. Cycles	Temperature Change °C
Initial	5		RT* to +100
Cycle	10 10	5	+100 to -100 -100 to +100
Final	5		+100 to RT

* RT = Room Temperature

The results of the test are shown in Table V. The cells with the integral coatings and the cells with the 6-mil conventional coverslides had CeO_2 and SiO intermediate, anti-reflective coatings, respectively. The coverslides were standard 6-mil OCLI* 7940 fused-silica with anti-reflective coating on the top surface and a 450-nm cut-on filter on the bottom surface. The bonding adhesive was General Electric RTV 602. The data were taken under a tungsten-light source with a substrate temperature of ± 1°C.

Both groups of cells showed an average increase in short-circuit current and open-circuit voltage. The charge in open-circuit could be attributed to the difference in the substrate temperature between the initial and post-test set-up, except for cell No. 105 which decreased 8 mV. The temperature coefficient of open-circuit voltage of the cells is approximately -2.3 mV/°C. All of the cells on the test, except No's. 102 and 104, showed little change in current at 430 mV. Cells No. 102 and 104, both of which had 1.0-mil integral coatings, changed +7.4 and -6.1 mA, respectively at 430 mV. Examination of the I-E curves of the cells indicated a change in series resistance of these two cells.

3. Proton Irradiation

Proton testing is tentatively scheduled for the third quarter of the contract on cells with integral coatings up to 6-mil thickness. A PN 400 Van de Graaff accelerator at Southern Methodist University has been modified for this test. An analyzing magnet and rotating substrate holder were added to the system to assure mono-energetic protons of uniform flux density. The system has been calibrated by bombarding a lithium target with protons and observing the resonance gamma-ray spectrum at various ion energies. The testing will be performed at 440 KeV.

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* Optical Coating Laboratory, Inc.

Table V. Electrical Results of Thermal Cycle Test

Cell No.	Description	I_{SC} (mA)			I at 430 mV (mA)			V_{OC} (mV)		
		Initial	Post-Test	Δ	Initial	Post-Test	Δ	Initial	Post-Test	Δ
101	Integral 1.9 mils	59.5	60.5	+1.0	51.1	52.3	+1.2	548	548	0
102	Integral 1.0 mils	56.0	57.5	+1.5	48.1	55.5	+7.4	541	543	+2
103	Integral 1.4 mils	59.6	60.8	+1.2	51.2	52.0	+0.8	543	541	-2
104	Integral 1.0 mils	60.2	61.0	+0.8	51.0	44.9	-6.1	544	540	-4
105	Integral 1.4 mils	59.5	60.5	+1.0	49.2	48.6	-0.6	540	532	-8
Average		59.0	60.1	+1.1	50.1	50.6	+0.5	543	541	-2
1	6-mil Coverslide	58.2	58.5	+0.3	47.5	47.5	0	530	528	-2
3	6-mil Coverslide	58.3	59.0	+0.7	49.0	49.0	0	534	530	-4
4	6-mil Coverslide	58.7	59.0	+0.3	48.5	49.1	+0.6	536	534	-2
5	6-mil Coverslide	57.6	58.3	+0.7	51.0	51.3	+0.3	531	532	+1
6	6-mil Coverslide	58.5	59.5	+1.0	48.0	48.7	+0.7	533	533	0
Average		58.3	58.9	+0.6	48.8	49.1	+0.3	533	532	-1

F. SAMPLE FABRICATION

The five samples supplied for the second quarter of the contract consisted of the following:

1) Substrate: N/P silicon solar cell, 1 x 2 cm, three-grid, 7 to 14 Ωcm base resistivity, solderless contacts.
2) Anti-reflective coating ($Si-SiO_2$): Cerium Dioxide
3) Integral coverglass: Corning 7940 fused-silica, 1-mil thickness
4) Anti-reflective coating (SiO_2-air): None

The I-E characteristic of sample cell No. 52 after integral coating is illustrated in Figure 11. The curve was plotted under 100 MW/cm^2 tungsten-light source, calibrated with Table Mountain standard No. 3.

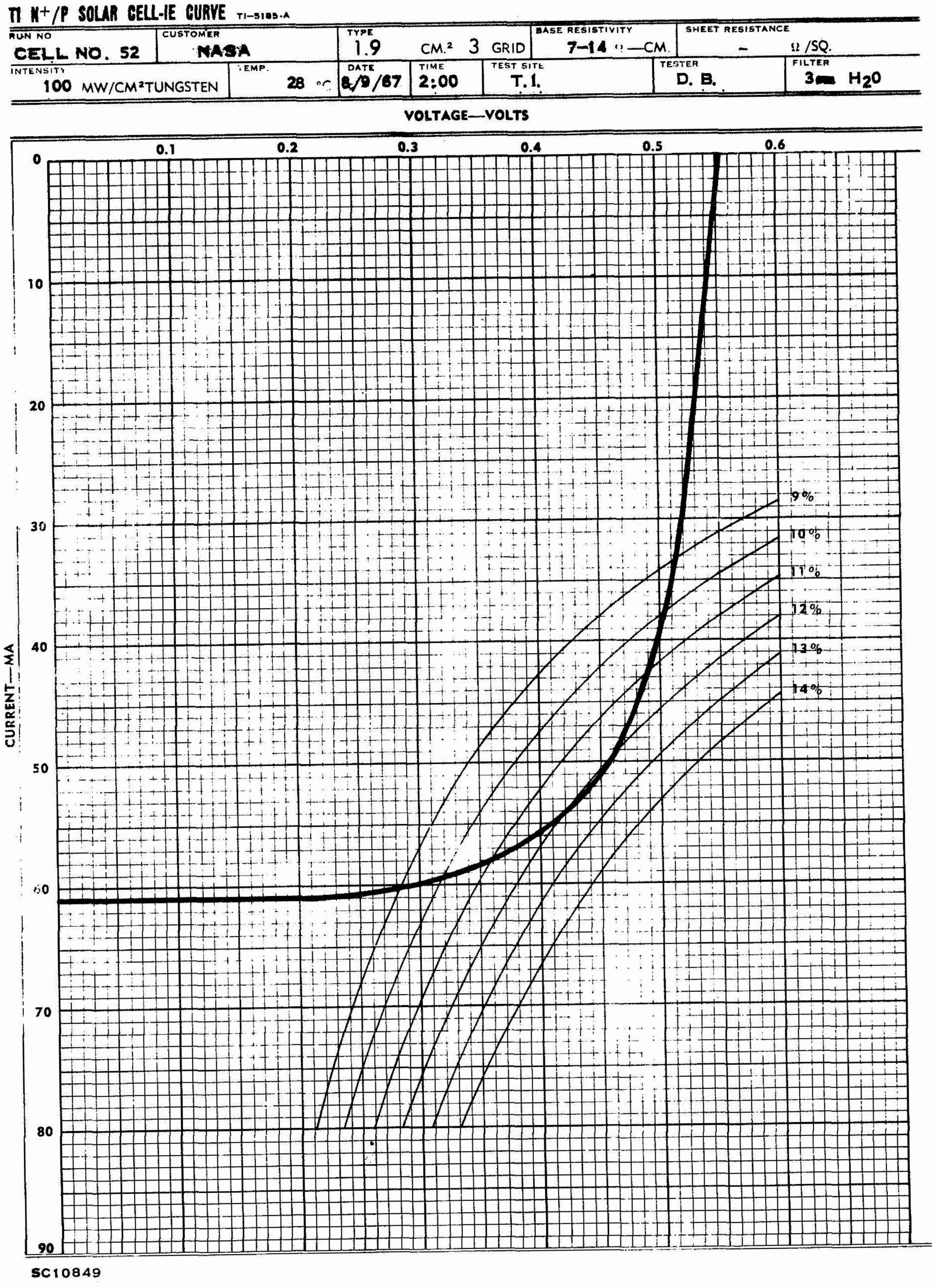

Figure 11. Solar-Cell I-E Characteristic After Integral Quartz Coating

SECTION III
PROGRAM FOR NEXT THREE MONTHS

Work will be directed at depositing and environmentally evaluating coatings in the 3- to 10-mil range. Stress measurements will also be extended for these thicker films. Proton testing is tentatively scheduled for the next reporting period.

SECTION IV
CONCLUSIONS

Integral quartz films, RF-sputtered on silicon solar cells, are proving to be very stable under the required environmental conditions; however, additional testing must be performed on films in the 3- to 10-mil thickness range.

Optimization of the intermediate, anti-reflective coating has potentially yielded a cell of higher conversion efficiency after integral coating than the standard, silicon-monoxide-coated cell without protective cover.

Stress measurements on films up to 4.16-mil thickness have been reported. The resultant curvature does not appear to be a significant problem on 13-mil silicon cells with 1- to 2-mil sputtered quartz. However, the curvature of cells with thicker films may cause problems in module and panel fabrication. The stress of the film seems to be relatively independent of the deposition rate, at least in the 1000-to-2400 Å/min range.

RF-sputtered quartz films currently can be deposited at the rate of 0.57 mil/hr with excellent physical and optical qualities. Studies are continuing on the deposition variables to further increase this rate.